

Scaling of Steel at Elevated Temperatures by Reaction with Gases and the Properties of the Resulting Oxides

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SCALING OF STEEL AT ELEVATED TEMPERATURES BY REACTION WITH GASES AND THE PROPERTIES OF THE RESULTING OXIDES

BY D. W. MURPHY, W. P. WOOD AND W. E. JOMINY

Abstract

This paper presents the results of an investigation of the variables affecting the oxidation of steel in the temperature range 1095 to 1316 degrees Cent. (2000-2400 degrees Fahr.) and shows that the effect of complex atmospheres on steel may be predicted from a knowledge of the equilibria in the systems $\text{Fe}:\text{O}:\text{C}$ and $\text{Fe}:\text{O}:\text{H}$. The results of this study may be summarized as follows:

1. *The loss in weight of the metal due to scaling is proportional within limits to the area of the sample,*

2. *The effect of increasing the carbon content in the range 0.3 to 1.1 per cent decreases the scaling losses,*

3. *The scaling loss is lessened by a slow rate of the flow of gas,*

4. *The rate of oxidation decreases as the time of exposure increases,*

5. *The extent of oxidation is dependent on the relative rates of diffusion of the gases concerned in the reaction,*

6. *A new method has been applied to the determination of equilibria in the reactions, $\text{FeO} + \text{H}_2 \rightleftharpoons \text{Fe} + \text{H}_2\text{O}$ and $\text{FeO} + \text{CO} \rightleftharpoons \text{Fe} + \text{CO}_2$ in the temperature range of 1093 to 1427 degrees Cent. (2000 to 2600 degrees Fahr.),*

7. *The melting point of ferrous oxide was determined from the data on the two systems at 1360 ± 10 degrees Cent. (2480 ± 18 degrees Fahr.)*

8. *The heat of fusion of ferrous oxide was calculated as 28,000 calories per gram mol $\pm$ 5,000 calories,*

9. *X-ray data have shown that ferrous oxide is*

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stable above its melting point having a constant 4.289 A. U. both above and below the melting point,

10. No evidence of extensive solid solutions of Fe or of Fe_3O_4 in FeO was obtained in this investigation,

11. The scaling or non-scaling action of a gas atmosphere containing nitrogen, carbon dioxide, carbon monoxide, hydrogen, and water vapor may be predicted with considerable accuracy for a number of steels on the basis of the equilibrium ratios derived for the two systems Fe: FeO: CO: CO_2 and Fe: FeO: H_2 : H_2O .

THE oxidation of steel or iron by reaction with gases is an interesting problem for both theoretical and applied research. A considerable amount of work has been done in connection with this general problem but in the main the results have shown a lack of concordance. In most cases such data as were available were obtained at temperatures below 1035 degrees Cent. (1900 degrees Fahr.) which is under the temperature ordinarily used in forging practice. The present research was undertaken at the instigation of The American Gas Association for the purpose of thoroughly investigating the scaling of steel throughout the complete forging range.

The problem has naturally divided itself into two parts:

(a). The investigation of the variables which control the process of continuous oxidation; namely, velocity of the gas stream, time, temperature, and gas composition. In addition a brief study was made of the effect of chemical composition on the scaling of steel particularly with reference to carbon.

(b). The determination of equilibria in the systems Fe: FeO: CO: CO_2 and Fe: FeO: H_2 : H_2O from which the effect of any gas-air combustion atmosphere can be predicted. In this connection various steels were subjected to scaling and non-scaling atmospheres, and the effects of these atmospheres were compared with those theoretically deduced from the equilibria determinations in order to prove definitely that the direction of the effect of the gas-air combustion atmosphere on steel may be predicted from the analysis of the atmosphere. The following pages are devoted to a brief review of the significant literature, an account of the procedure followed in this research, and to a discussion of the results obtained.

REVIEW OF LITERATURE

Previous investigations of the oxidation of iron and ferrous alloys fall into three general classes. The first and oldest of these is concerned with the determination of the various equilibria in the systems $\text{Fe}:\text{O}:\text{H}$ and $\text{Fe}:\text{C}:\text{O}$. The second class includes a number of more or less empirical researches whose object generally was to ascertain the oxidizing effect of various gases, chiefly air on specific metals. Such researches have for the most part entirely disregarded many of the variables which enter into the oxidation process. The third class of investigations are those few in which attempts were made to deduce possible mechanisms for continued oxidation. In the latter two classes the variables considered have been limited in number, and no comprehensive study of these various factors has been made.

The first published record of investigations in these systems was that by Deville¹ in 1870. He studied the qualitative aspects of the system $\text{Fe}:\text{O}:\text{H}$. Following this original work of Deville, a number of researches were made in which his experimental method with few changes served as the basis. The method employed by Deville and later investigators consisted essentially of heating iron-iron oxide mixtures in a porcelain or quartz tube in contact with the gas phase in a sealed system until equilibrium was reached at a constant temperature.

In the case of $\text{H}_2:\text{H}_2\text{O}$ equilibria the reaction tube containing the solid phases was connected with a reservoir containing water maintained at a constant temperature. The tube was evacuated to a pressure corresponding to the vapor pressure of water at the reservoir temperature. The reaction of steam and iron produced hydrogen which caused an increase of pressure in the system, which change in pressure was observed by means of a manometer which registered the total pressure. Heating at constant temperature was continued until the total pressure given by the manometer remained constant when equilibrium was considered to have been established. From the known vapor pressure of water and the total pressure in the system, the pressure and consequently the percentage of hydrogen were calculated. In the case of the $\text{Fe}:\text{O}:\text{C}$ system the gas phase, carbon dioxide, or carbon monoxide, depending on the desired direction of approach to equilibrium, was introduced into an evacuated

¹Deville, *Comptes Rendus*, Vol. 70, p. 1105, 1210 (1870), also Vol. 71, p. 30 (1870).

tube containing the solid phase until atmospheric pressure was attained. After certain periods of time, samples of gas were withdrawn and analyzed; equilibrium was considered as established when no variation in composition occurred with increasing time.

Eastman² in 1922 reviewed the available literature in the Fe:O:H and Fe:O:C systems. He noted that in general the results of preceding investigations of the Fe:O:H system fell into two groups differing by as much as 40 to 50 per cent in values of the equilibrium constant, and yet there appeared to be little reason for choosing one set in preference to the other on the basis of experimental procedure. Consideration of this system in conjunction with the Fe:O:C system led Eastman to postulate the existence of solid solutions over a considerable range of oxygen content instead of definite constant solid phases as an explanation of the discrepancies existing between the two groups of data. Later his investigation with Evans³ seemed to confirm those showing high values of the constant. The apparent reliability of his results with the Fe:O:H system led to questions concerning the reliability of the accepted constants for the water-gas reaction as determined by Haber,⁴ Hahn,⁵ and others when his data were combined with data on the Fe:C:O system in the indirect calculation of these constants.

Neumann and Kohler⁶ in 1928 in a careful and thorough research on the direct determination of the water-gas equilibrium, established the constants of that reaction with considerable precision, and agreed substantially with the previous direct determinations. The results of the indirect calculation from the Fe:C:O and Fe:O:H systems pointed to weaknesses in the Fe:H:O determinations. The work of Krings and Kempkens,⁷ of Tritton and Hanson,⁸ and of Herty,⁹ which has definitely limited the possible solid solutions of

²Eastman, *Journal*, American Chemical Society, Vol. 44, 1922, p. 975.

³Eastman and Evans, *Journal*, American Chemical Society, Vol. 46, 1924, p. 888.

⁴Haber, *Zeitschrift fuer Anorganische und Allgemeine Chemie*, Vol. 38, 1904, p. 5.

⁵Hahn, *Zeitschrift fuer Physikalische Chemie*, Vol. 44, 1903, p. 5131 and Vol. 48, 1904, p. 735.

⁶Neumann and Kohler, *Zeitschrift fuer Elektrochemie und Angewandte Physikalische Chemie*, Vol. 34, 1928, p. 218.

⁷Krings and Kempkens, *Zeitschrift fuer Anorganische und Allgemeine Chemie*, Vol. 183, 1929, p. 225.

⁸Tritton and Hanson. *Journal Iron and Steel Institute*, Vol. 110, 1924, p. 85.

⁹Herty, et al. "Physical Chemistry of Steel Making," Carnegie Institute Technology, Bulletin 34, 1927.

Fe and FeO has seemed to disprove the possibility of extensive solid solutions as an explanation of the discrepancies existing in the data on the Fe:O:H system.

Emmett and Schultz¹⁰ in 1930 published the results of their research in which a flow method somewhat similar to that of Ferguson was used. Their method consisted of passing steam-hydrogen mixtures over iron-iron oxide mixtures and then collecting the effluent gases for a certain period of time and determining the relative quantities of water and hydrogen. The analyses were repeated many times at each temperature starting with steam-hydrogen mixtures for both reducing and oxidizing conditions and thus a high degree of accuracy was insured. The excellent agreement of their work when combined with data on the Fe:C:O system in indirect calculation of the water-gas constants with the direct determinations of Neumann and Kohler, seems to be substantial proof of the validity of their work.

Eastman,² in his review of the literature found that the data on the Fe:C:O system were somewhat more concordant than was the case in the Fe:H:O system. He was inclined to place considerable weight on the determinations of Matsubara¹¹ in spite of the questionable temperature measurements of that author. Garran¹² attempted to carry the experimental data to a temperature of 1300 degrees Cent. (2370 degrees Fahr.) but impurities, chiefly about 2 to 3 per cent siliceous matter, present in his original iron rendered his work very doubtful. Schenck,¹³ in a series of papers reported the results of extensive determinations in this system. He pointed out that a considerable number of impurities have a decided effect on the equilibria in this system, and his work shows that where these have not been considered the results are of very questionable value. In view of the care with which this research has been carried on and the general consistency of his results it seems quite likely that his recent data are the most acceptable that has yet appeared.

The empirical researches which were chiefly concerned with oxidation of specific materials are quite numerous. The data pre-

¹⁰Emmett and Schultz, *Journal*, American Chemical Society, Vol. 52, 1930, p. 4268.

¹¹Matsubara, *Transactions*, American Institute of Mining and Metallurgical Engineers, Vol. 67, 1922, p. 3.

¹²Garran, *Transactions*, Faraday Society, Vol. 24, 1928, p. 201.

¹³Schenck, et al., *Zeitschrift fuer Anorganische und Allgemeine Chemie*, Vol. 167, p. 315; Vol. 166, p. 113; Vol. 167, p. 254, 1927.

sented in these empirical researches are not extremely concordant and include a number of scattered observations. The early authors, Scott,¹⁴ McCormick,¹⁵ Stead,¹⁶ and Dickenson,¹⁷ used crude methods for determining the extent of oxidation; scale was removed by abrasion which must, of course, have removed also an indeterminate quantity of iron; conditions of purity of gases, temperature control, and other factors such as the velocity of the gas stream were inadequately controlled. The later authors, Cobb¹⁸ and his associates, Utida and Saito¹⁹ and Hatfield,²⁰ based their measurements on gain in weight which method is much more reliable than the methods previously used. It has the difficulty though, of failing to give a clear conception of the quantity of metal lost since the oxides may vary in composition under different conditions of temperature and atmosphere and with different compositions of original material. Furthermore, most of these results are rendered incomparable since one variable, velocity of the gas stream, has been almost wholly neglected. Further observations on this point will be made subsequently.

Several attempts have been made to outline a possible mechanism for the continued oxidation of a metal, and these attempts comprise the third class of researches. Jordis and Rosenhaupt²¹ in 1908 advanced the following hypotheses to explain surface oxidation: (a) The oxygen may dissolve in the metal as such or as an alloy; (b) the oxygen may diffuse through the layer of oxide which may dissolve the oxygen or merely be porous to it; (c) oxygen may be carried by the alternate formation of higher and lower oxides; or (d) the oxide may fall from the surface of the metal. Most of the ideas subsequently advanced by other authors are in support of one of these hypotheses. Friend²² advanced the hypothesis that oxida-

¹⁴Scott, *Chemical and Metallurgical Engineering*, Vol. 25, 1921, p. 72.

¹⁵McCormick, *TRANSACTIONS, American Society for Steel Treating*, Vol. 2, 1922, p. 1006.

¹⁶Stead, *Journal, Iron and Steel Institute*, 1916; *Engineering*, Vol. 102, 1916, p. 367.

¹⁷Dickenson, *Journal, Iron and Steel Institute*, 1922; *Engineering*, Vol. 114, 1922, pp. 326-9.

¹⁸Cobb, et al., *Journal, Society of Chemical Industry*, Vol. 46, 1927, p. 61 T, p. 68 T.

¹⁹Utida and Saito, *Science Reports, Tohoku Imperial University*, Vol. 13, 1925, p. 391.

²⁰Hatfield, *Journal, Iron and Steel Institute*, 1927, p. 483.

²¹Jordis and Rosenhaupt, *Zeitschrift fuer Angewandte Chemie*, Vol. 21, 1908, p. 50.

²²Friend, *Journal, Iron and Steel Institute*, Vol. 80, 1909, p. 172. *Journal, West Scotland Iron and Steel Institute*, Vol. 17, 1910, p. 66. *Proceedings, Chemical Society*, Vol. 27, 1911, p. 124. *Journal, Chemical Society*, Vol. 99, 1911, p. 969.

tion in the case of steam was carried on in the following manner. Steam first dissociates into hydrogen and oxygen. The oxygen thus liberated, oxidizes the metal to FeO and later to Fe_3O_4 . Continued oxidation is then carried on by alternate reduction and formation of this latter oxide.

Pilling and Bedworth²³ studied rather extensively the oxidation of copper in air at various temperatures and for various times. They classified metals as noble or base, depending on the magnitude of the dissociation pressure of the oxide which for the noble metals is so high even at low temperatures as to preclude oxidation. The base metals they divide into two groups depending on the oxide texture which determines whether or not the oxide coating will retard further oxidation. They interpreted their data as showing that continued oxidation of a metal resulted from the solution and diffusion of oxygen through the oxide layers. Their investigation of the various factors was somewhat incomplete since they omitted such considerations as velocity and composition of the gas stream.

Fedotjev and Petrenka²⁴ favor the transfer of oxygen by means of the alternate formation of higher and lower oxides. According to this mechanism one of the higher oxides, Fe_2O_3 or Fe_3O_4 is first formed, and this is subsequently reduced by the iron in contact with it to FeO , additional iron being oxidized in this process. The FeO is then oxidized to a higher oxide and the reaction continues.

Pfeil²⁵ in 1930 published an account of his experiments as a result of which he advanced the idea that in addition to oxygen diffusing inward through the scale, iron in some form must also diffuse outward. He also established the fact that two scales of different oxygen contents can react even when not actually in contact with each other. As proof that there must be a diffusion of iron outward, he cited the following facts. The scale as it forms begins to surround foreign objects and may eventually cover them up without, however, disturbing their initial position; the original markings on the test samples are preserved in relief on the middle portion of the scale in the same position they had on the original sample. These facts taken in conjunction, preclude any possibility of plastic flow to

²³Pilling and Bedworth, *Journal*, Institute of Metals, 1923.

²⁴Fedotjev and Petrenka, *Zeitschrift fuer Anorganische und Allgemeine Chemie*, Vol. 157, 1926, p. 165.

²⁵Pfeil, *Journal*, Iron and Steel Institute (1930).

account for growth of the scale outward, and the diffusion of iron will explain the development of the large oxide crystals in some cases. As the mechanism exists now, continued oxidation is accompanied by a diffusion of iron outward and a migration of oxygen inward. This latter seems to occur partially as a result of the ability of scales or oxides of differing oxygen content to react with each other. This hypothesis seems to be the most acceptable in view of the facts as understood at present. There were some facts brought out in the present research which seemed to indicate that some modification of this hypothesis was necessary.

In concluding this survey of the literature it would be well to summarize a few points concerning the past work. There are no accurate data on the equilibria in the system $\text{Fe}:\text{C}:\text{O}$ above 1100 degrees Cent. (2010 degrees Fahr.) and none above 1000 degrees Cent. (1830 degrees Fahr.) in the system $\text{Fe}:\text{O}:\text{H}$. While extrapolation of data obtained at lower temperatures would be fairly reliable up to the melting point of the oxide, extension beyond this point involves guessing at the probable heat of fusion of the oxide. Furthermore, there has been no systematic investigation of the various factors which influence the process of scaling. It was hoped that this investigation would serve to bring these factors into proper relation to each other, and would indicate a comprehensive mechanism.

PROCEDURE

The apparatus used in this study is in most respects similar to that used by other investigators. The methods employed in the conduct of tests, however, differ considerably from those used previously. Both have been described in previous publications but a brief resumé will be of value.

Apparatus

The heating equipment used in this research consisted of a gas-fired muffle furnace in which a glazed porcelain tube having a 2-inch inside diameter was placed in such a manner that both ends of the tube projected some distance beyond the furnace walls. One end of the tube was fitted with an asbestos plug through which there were two holes, one for the thermocouple protection tube, and one for the introduction of the chosen gas. This plug was capped and held

in place with firebond cement which produced a tight joint. The other end of the tube through which the sample was introduced was provided with a rubber stopper since this end was sufficiently cool to prevent any decomposition of the stopper. Two types of thermocouple protection tubes were used, a sillimanite tube and a glazed closed-end porcelain tube. The thermocouple and its protection tube were so placed that the hot junction of the couple was approximately in the longitudinal center of the hot zone and about one-half inch above the axis of the tube. In this position the distance of the sample from the couple was always between one-quarter and one-half inch, the center of the sample being directly under the hot junction of the couple. The thermocouples used were platinum, platinum-rhodium and the voltage they developed was measured by a portable potentiometer graduated in tenths of a millivolt. The porcelain tube was protected from direct contact with the flame of the burners by a D-shaped carborundum muffle. To secure a uniform flow of gas in the tube, it was packed for a distance of about nine inches ahead of the inlet with porcelain chips.

Flowmeters of the ordinary friction type using mercury as the indicating fluid were used for the measurement of quantity in the case of the permanent gases, carbon dioxide, carbon monoxide, hydrogen, air and commercial illuminating gas. These meters were calibrated in terms of cubic feet per hour against a Sargent wet test meter for the specific gas to be used.

Steam for use in these runs was generated in a small boiler made of 4-inch steel pipe which contained an electric immersion heater. In addition, a smaller boiler was used for low rates of flow since the control of the large boiler was not sufficiently accurate for small outputs. It was necessary to free the steam from any gases dissolved in the water. This was accomplished in each of the boilers by allowing the water to boil vigorously for at least one-half hour and exhausting the steam to the air before connecting them to the furnace tube.

To introduce steam into a hydrogen stream, a saturator was assembled which consisted of five bottles, connected in series by glass tubing and well sealed. These were immersed in a water bath which could be maintained at constant temperatures within ± 0.1 degree Cent. The saturator was checked at various points in the range where it was to be used and was found to be accurate within 0.1 per

Table I
Chemical Composition of Steels

Steel	C	Mn	Si	Per Cent S	P	Ni	Cr	Va	Mo	W
Electrolytic Iron	0.012	0.008	0.001	0.007	0.002					
1015	0.19	0.53	0.18	0.020	0.016					
1030	0.28	0.653	0.01	0.032	0.013					
1050	0.52	0.64		0.034	0.025					
1090	0.88	0.34		0.018	0.029					
High Carbon Tool Steel	1.12	0.33	0.21	0.026	0.011					
2320	0.17	0.59	0.24	0.020	0.018	3.40				
3130	0.35	0.56		0.025	0.016	1.11	0.56			
6145	0.47	0.58	0.16	0.015	0.015		0.98	0.24		
4140	0.39	0.67		0.024	0.020		0.93		0.32	
4615	0.21	0.54	0.29	0.012	0.017	1.81			0.25	
High Speed Steel	0.73	0.32	0.08	0.018	0.025		4.27	1.06		18.62

cent. The gas to which water vapor was to be added was always passed through the saturator for about an hour before starting a series of experiments in order to eliminate gases which might have been dissolved in the distilled water used in the bubbling towers.

Carbon monoxide for use in the runs to determine the extension of the Fe: FeO: CO: CO₂ equilibrium was prepared by allowing formic acid to drop slowly into hot concentrated sulphuric acid. Carbon dioxide and hydrogen were obtained from tanks. All of these gases were purified by passing through absorption trains. For gas-air combustion atmospheres, air was taken from the laboratory line and gas from a pressure storage tank which had been filled from the city mains. This insured a source of gas having a constant composition.

The metals used are listed in Table I. The steel samples were prepared for use in 2-inch lengths and polished to a uniform brightness with 00 emery cloth. The electrolytic iron used was in the form of hollow cylinders having a $\frac{3}{8}$ -inch wall. These were polished in a manner similar to that of the steel samples.

Method

The procedure used in the scaling tests has been previously described in a paper in which two of the present authors²⁶ collaborated.

This procedure was applied also to the equilibria determinations

²⁶W. E. Jominy and D. W. Murphy, TRANSACTIONS, American Society for Steel Treating, Vol. 18, 1930, p. 19.

with hydrogen, steam, and carbon monoxide—carbon dioxide atmospheres. A weighed electrolytic iron cylinder previously described was mounted in the same fashion as the steel samples in the scaling tests and then introduced into the porcelain tube. The atmosphere in the tube had previously been adjusted to the desired ratio of steam to hydrogen or of carbon dioxide to carbon monoxide, and the sample was then exposed to the action of this moving atmosphere for a period of 30 minutes in the case of the steam-hydrogen experiments or for a period of one hour in the case of the carbon dioxide-carbon monoxide determinations. After this exposure the sample was withdrawn into a quenching bath of distilled water as described. The quenching, while it immediately stopped any scaling reaction at high temperatures, resulted in the formation of small amounts of oxide by reaction of the iron with water, particularly on samples which were unscaled in the chosen furnace atmosphere. But the amounts of oxide formed during the short quenching times on unscaled iron or steel were found to be approximately constant for any given temperature at which the metal was immersed.

In the case of steam-hydrogen runs, visual observation served to determine whether or not the sample had scaled in the chosen atmosphere, since the reaction, if it proceeded, gave an easily recognizable quantity of scale. This observation was subsequently checked by determining the loss in weight using the stripping methods outlined in the previous paper. Because the reaction was much slower when atmospheres of carbon dioxide and carbon monoxide were used, it was necessary when using these atmospheres to rely on weight determinations to ascertain whether the action of the atmosphere had been scaling or non-scaling. The composition of the gases flowing through the tube was then varied until two compositions were found whose contents of oxidizing gas differed by not more than 2 per cent when, at the same temperature, one produced scaling and the other did not. In some cases the difference between the contents of oxidizing gas in two atmospheres was as low as 0.5 per cent, but this small range was not the rule. In the preliminary experiments with carbon dioxide-carbon monoxide mixtures, the usual range between carbon dioxide contents of scaling and non-scaling mixtures was 2 per cent, but in the final experiments this range was decreased to 0.6 per cent. The differentiation between scaled and non-scaled sample was very sharp even with this reduced range, and the method is, consequently,

thought to be very sensitive. Fig. 5 is a typical illustration of the data secured and shows the marked increase in oxidation which occurs when the atmosphere becomes slightly oxidizing. At temperatures of 1370 and 1425 degrees Cent. (2500-2600 degrees Fahr.) where the oxide is liquid, it was necessary to alter the method of mounting these samples. Boats were fabricated from a chromium oxide cement to contain two sillimanite crossbars. The boat was brought to the temperature of the furnace and the sample then placed on the two sillimanite bars. At the termination of the run it was only necessary to remove the sample, since one boat was sufficient for several heats. The rest of the procedure at these temperatures was entirely similar to that at lower temperatures.

In order to maintain a check on the condition of the tube, and to check the composition of gaseous mixtures, it was necessary to make gas analyses. The apparatus used for analysis was a modified Orsat which had provision for the determination of carbon dioxide, oxygen, carbon monoxide, hydrogen, unsaturated hydrocarbons, and hydrocarbons of the methane series.

The total error that may be expected in individual measurements of scaling appeared to be about ± 2.5 per cent which would indicate a possible variation of 5 per cent between individual runs under like conditions. In the case of determinations of the equilibria in the $\text{Fe}:\text{O}:\text{H}$ and $\text{Fe}:\text{C}:\text{O}$ systems, the only matter of interest was the question of whether or not the sample had scaled. The results were therefore not sensitive to time errors nor to some of the weight errors, since the question of rate of oxidation was not involved. The chief errors then are those of temperature measurement and gas composition. It has been estimated that the temperature errors may be ± 0.5 per cent while the composition errors may be ± 0.2 per cent, making a total error of ± 0.7 per cent in each individual determination. In a later portion of this paper the possible sources of uncertainty in drawing the curves will be reviewed.

DISCUSSION OF RESULTS

The variables in the process of the oxidation of iron are the effect of variation of velocity of the gas stream, the effect of variation of the temperature at which the steel is exposed, the effect of variation of time of exposure, the effect of variation of the carbon content of the steel, and the effect of variation of size. The data on variation

of time, temperature, and velocity in atmospheres of dry air, carbon dioxide, and steam were presented in a paper by W. E. Jominy and D. W. Murphy²⁶, previously referred to. These data are reproduced in the curves of Figs. 1, 2, and 3. No discussion of scaling would be complete without reference to the effect of atmosphere. However,

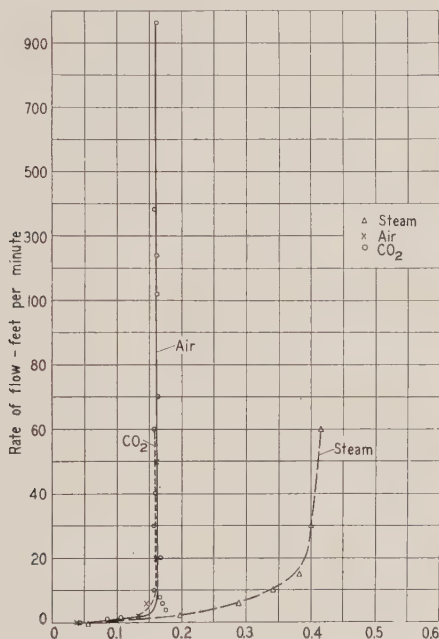


Fig. 1—Effect of Variation of Velocity of Gas on the Scaling of S.A.E. 1015 Steel at 1250 Degrees Cent. (2280 Degrees Fahr.).

the study of this effect is exceedingly difficult when the products of combustion of city gas and air are chosen as the atmosphere. It will be shown that this problem is considerably simplified by the application of data obtained in the study of equilibria in the systems Fe: FeO: CO: CO₂ and Fe: FeO: H₂ and H₂O. The investigation of these systems at temperatures over 1000 degrees Cent. (1832 degrees Fahr.) has led to some interesting and important information connected with the melting of ferrous oxide. The data for the Fe: FeO: H₂: H₂O system was presented in a recent paper by Jominy and Murphy²⁷ and Figs. 6 and 8 are reproductions of that data.

²⁷Jominy and Murphy, *Journal of Industrial and Engineering Chemistry*, Vol. 23, 1931, p. 384.

Effect of Area

The data of Table II show quite conclusively that the oxidation process is a surface phenomenon as it is quite evident that the scaling loss is proportional to the area of the sample. However, there must be a limiting size of sample below which the mass of metal will enter as a factor. This arises from the fact that the reaction in question,

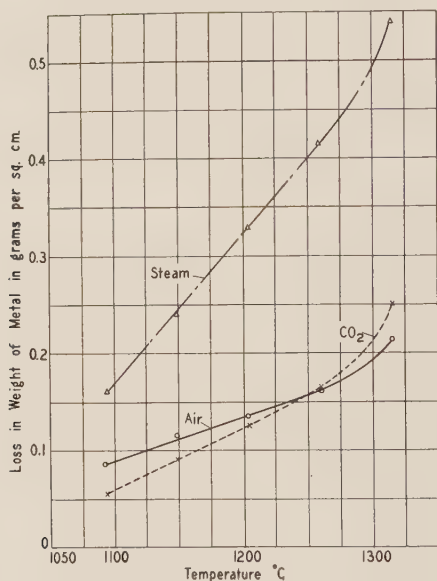


Fig. 2.—Effect of Variation of Temperature on the Scaling of S.A.E. 1015 Steel in Various Gases.

$3\text{Fe} + 2\text{O}_2 \rightarrow \text{Fe}_3\text{O}_4$, is exothermic. Hence, there will be a tendency as the size of the sample is decreased for the development of heat to increase the temperature of the sample, and, consequently, to increase the rate of reaction. In all cases, however, where the heat resulting from the surface reaction is not concentrated on a relatively small mass, the reaction will proceed as a strictly surface phenomenon, and the amount of metal lost by oxidation will be proportional to the area of the sample. The limiting size, below which the loss of metal by oxidation would cease to be proportional to the area, is not definitely known, and, furthermore, it would vary for different temperatures inasmuch as the concentration of heat is partly dependent on the initial reaction rate. The fact that the scaling loss is proportional to the area

does not offer any clue to the mechanism since it means simply that the active mass of iron concerned in the reaction is solely in the surface layer.

Effect of Carbon Content

It is apparent from a consideration of the data presented in Table III and Fig. 4 that the effect of the carbon content of the steel is rather capricious at 0.5 per cent and below. It will be noted that the loss of metal by scaling is definitely decreased in the high carbon

Table II
Effect of Variation of the Size of Sample on Scaling of SAE 1015 Steel in
Dry Air at 1260 Degrees Cent.

Sample Number	Total Time in Furnace, Minutes	Rate of Flow Feet per Minute	Diameter of Sample in Inches	Per Cent Loss in Weight	Loss in Grams per sq. cm.	Wt. of Scale in Grams per sq. cm.	Av. Loss in Wt. Av. Wt. of Scale
AR7	40	60.0	0.500	7.96	0.1753	0.2428	
AR8	40	60.0	0.500	7.58	0.1672	0.2366	
Average				7.77	0.1712	0.2397	0.715
AR9	40	60.0	0.375	9.65	0.1647	0.2400	
AR10	40	60.0	0.375	9.99	0.1753		
Average				9.82	0.1700	0.2400	0.709
AR11	40	60.0	0.6197	6.86	0.1829	0.2554	
AR12	40	60.0	0.6230	6.66	0.1787	0.2480	
Average				6.76	0.1808	0.2517	0.719
630	40	60.0	0.8138	4.88	0.1675	0.2320	
646	40	60.0	0.8135	5.18	0.1728	0.2406	
Average				5.03	0.1701	0.2363	0.720

range. Scott¹⁴ has attributed this to the preferential oxidation of carbon. There is also another possibility which would account for the decreased scaling loss in dry air in the high carbon steels. It would be expected that the carbon of the steel would be oxidized to carbon monoxide which being present within the scale would have a tendency to retard the oxidizing action. An examination of the ratio column of this table shows that the proportion of FeO in the scale is increasing as the carbon content increases; that is the ratio begins to deviate from 0.724 for Fe_3O_4 toward 0.777 for FeO. This could occur only if the oxidation of FeO to Fe_3O_4 was partially prevented by carbon monoxide. Hence, as the carbon content of the steel increased, the magnitude of the opposing tendency also increased with the net result that the speed of reaction was decreased. In general

this is the effect noted, although the operation of this factor is certainly not pronounced in low carbon steels.

Effect of Velocity

One of the most interesting features of the data shown in Fig. 1, in which the velocity of various gases was varied, is that as the velocity of the stream is increased a constant loss is attained which

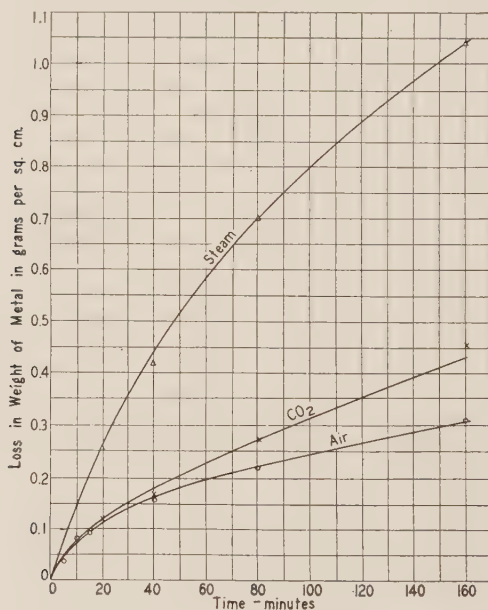


Fig.3—Effect of Variation of Time Exposure on the Scaling of S.A.E. 1015 Steel at 1260 Degrees Cent. (2300 Degrees Fahr.).

does not appear to be affected by a further increase in velocity. There is no probable mechanism of continued oxidation of a metallic surface which does not include migration of oxygen inward through the scale after the first oxidation has occurred. If no such transfer of oxygen were present, the process of oxidation would be considerably inhibited since it could only take place upon iron which had diffused outward provided the scale remained intact on the surface. Even the various theories in which higher oxides are regarded as oxygen carriers in reality reduce to a diffusion phenomenon for in this case the inward diffusion of oxygen is accomplished by the alternate formation and

Table III
Effect of Variation of Carbon Content on the Scaling of Steel
at 1260 Degrees Centigrade in Dry Air.

Run No.	Steel	Per Cent Carbon	Veloc-ity of Air		Loss in Weight Per Cent	Loss in Weight Gms. per sq. cm.	Weight of Scale Gms. per sq. cm.	Ratio Loss in Wgt. Wgt. of Scale
			Ft. per Minute	Time Minutes				
338	1015	0.18	60	40	4.86	0.1640		
630	1015	0.18	60	40	4.88	0.1675	0.2320	0.723
avg.					4.87	0.1657		
A1-21	1030	0.28	60	40	8.09	0.2485	0.3520	
A1-22	1030	0.28	60	40	7.91	0.2455	0.3420	
avg.					8.00	0.2470	0.3470	0.712
A2-18	1050	0.52	60	40	7.35	0.2320	0.3240	
A2-19	1050	0.52	60	40	6.65	0.2100	0.2840	
avg.					7.00	0.2210	0.3040	0.727
A3-17	1090	0.88	60	40	6.35	0.2000	0.2720	
A3-18	1090	0.88	60	40	6.30	0.1980	0.2700	
avg.					6.33	0.1990	0.2710	0.735
E-18	High C	1.12	60	40	4.99	0.1790	0.2395	
E-19	High C	1.12	60	40	4.62	0.1652	0.2200	
avg.					4.80	0.1721	0.2298	0.750

reduction of higher oxides. Since any plausible mechanism must provide for diffusion of the oxidizing agent through the scale, the question of supply of the oxidizing agent must occur. Admittedly, the supply of oxygen is dependent on the velocity of the gas stream which must replenish the oxidizing agent absorbed by the reaction from the film of gas surrounding the metallic sample. From this reasoning it appears that rates of flow of gas must exist which cannot maintain the supply of oxidizing agent at a sufficient level to satisfy the requirements of the reaction at the particular temperature being studied. Likewise, it is evident that when the rate of supply becomes equal to the maximum rate at which the oxidizing agent is used at the temperature in question, the reaction proceeds to its full extent and no further increase in rate of supply can alter the amount of metal entering the oxidizing reaction. The characteristics of the curves of Fig. 1 evidently fulfill this conception. First, then, to secure comparable results on rates of oxidation, it is necessary to carry on the experiments in a range of velocity where the supply of the oxidizing agent is assuredly more than equivalent to the rate at which this agent can be used. For this reason observations of scaling rates in this work have been carried on with rates of flow of 60 feet per minute, a rate which seems to insure ample supply.

Effect of Temperature

Temperature, of course, has a pronounced effect on the rate of

oxidation of steel, as is clearly demonstrated in Fig. 2. The curves in the region covered in this research seem to be nearly linear until the melting point of the oxide is attained. The sharp break which occurs in all the curves above 1316 degrees Cent. is additional evidence that the degree of continued oxidation is conditioned upon the protective action of the scale. Since the melting point of the oxide scale lies below 1370 degrees Cent. (2500 degrees Fahr.) the scale

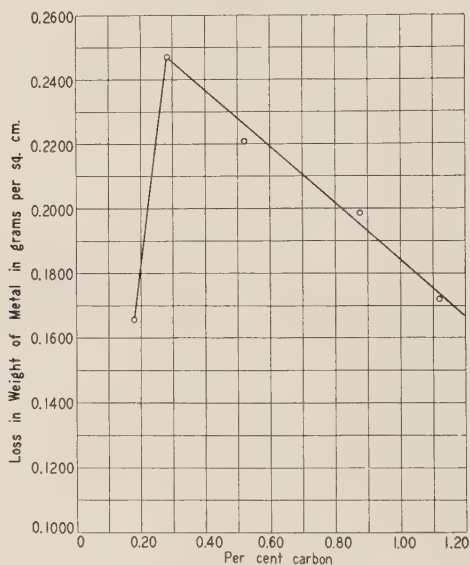


Fig. 4—Effect of Variation of Carbon Content of Steel on the Scaling in Dry Air at 1260 Degrees Cent. (2300 Degrees Fahr.).

must exist in a molten condition at this latter temperature, and in the molten state its protective action against further oxidation is destroyed. The empirical expressions for the curves of Fig. 2 are easily established for the range 1093 to 1316 degrees Cent. (2000-2400 degrees Fahr.) according to the general form $W = A + BT$, where W is the loss in weight in grams per square centimeter for 40 minute runs, T is the temperature in degrees Centigrade, and A and B are constants. For the three gases dry air, steam, and carbon dioxide, the data from 1093 to 1316 degrees Cent. (2000-2400 degrees Fahr.) may be expressed as follows: for air $W = 0.000455T - 0.4118$; for steam, $W = 0.001539T - 1.5244$; and for carbon dioxide, $W = 0.000638T - 0.6375$.

Effect of Time

From the form of the curves of Fig. 3 where loss in weight per square centimeter is plotted against time, it is apparent that the rate of oxidation is diminished as time is increased. Since the mechanism must involve diffusion of the oxidizing gas through an increasing thickness of scale, it is evident that this diffusion factor will operate to reduce the rate of oxidation as the time of exposure increases. For air the data for 1260 degrees Cent. (2300 degrees Fahr.) yield the equation $W^2 = 0.000604t$, where W is the loss in weight per unit of area, and t is the total time in the furnace in minutes.

The data with steam and carbon dioxide are not so easily reduced to empirical formulae. The results with steam are well expressed by an equation of the type $W^2 = kt + b$. This type is bound to fail for short times because of the constant "b". Evaluation of the constants yields the expression: $W^2 = 0.007371 t - 0.0986$. It is evident that with this type of equation representing the data at 1260 degrees Cent. there is insufficient data in Table VI to permit a calculation of the reaction constants at the various temperatures. The data for carbon dioxide are best expressed by the equation $t = (26.86 W + 1.605)^2$. To determine the weight, — time, — temperature equation would in this case, also, require more data than that presented in Fig. 2. The rate of oxidation unquestionably falls off as time increases.

The Mechanism of Oxidation

Pfeil²⁵ in his excellent research established the fact that oxides of high oxygen content will react with oxides of lower oxygen content even when the oxides are not actually in contact. But this reaction is without doubt very slow according to the times he used to establish the trend of the reaction, and, consequently, no great amount of oxidation would result by this means. But his chief addition to the theory of the mechanism of scaling was that in addition to the oxygen diffusing inward through the scale, the iron must also diffuse outward through the scale.

In support of his theory that iron must also diffuse outward, Pfeil cited several phenomena, among the most interesting of which was the occurrence of punch markings within the body of the scale. These markings originally present on the surface of the steel were

preserved in relief in their original outline at a position which corresponded with the initial dimensions of the steel sample. The relief figures were evident in the middle portion of the scale and accordingly were not visible on the outside or the inside when the scaling process had been carried on for a sufficient length of time to diminish considerably the dimensions of the sample. The fact that the figures

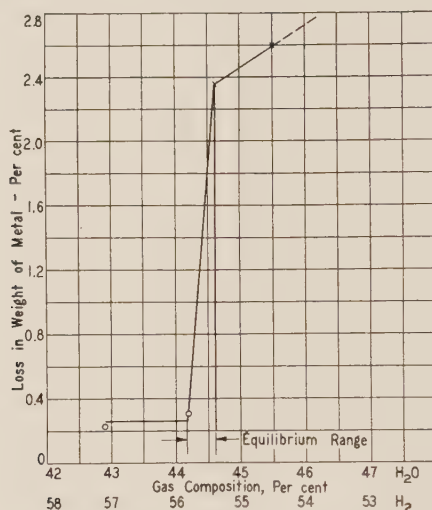


Fig. 5—Effect of Small Variations of Gas Composition Near the True Equilibrium Range on the Loss in Weight of Iron Samples at 1260 Degrees Cent. (2300 Degrees Fahr.). Data from Fe-O-H System.

were built in relief and were imbedded in scale at their original position could only be explained by the outward diffusion of iron. Obviously any plastic flow in the scale would cause at least a distortion, if not a total disappearance, of any figures arising from the original configurations on the surface of the steel. This phenomenon cited by Pfeil has been confirmed in the present work

The mechanism of solid diffusion seems to involve the assumption that the diffusing solid shall first dissolve in the solid through which it must diffuse. The driving force for diffusion must then depend on a difference in concentration of the diffusing solid between that portion of the solid solution which is in immediate contact with the diffusing solid, and which may be considered as saturated with respect to that solid and the main portion of the solid solution. Thus,

if there were no possibility of maintaining the main portion of the solid solution in an unsaturated state with respect to the diffusing solid, the diffusion would cease when the whole portion of the solid solution had become saturated. The oxidizing power of a certain gas would then be partly conditioned on the ease with which it would maintain the main portion of the oxide scale in an unsaturated condition with respect to iron; and this in turn is dependent on the speed with which the gas molecules can diffuse into or permeate the main portion of the oxide. Of course, the maintenance of a continuous diffusion of iron outward would also necessitate at all times an oxide-metal interface, since, if this interface were destroyed, no iron could be withdrawn from the main body of the metal except as vapor which would be highly improbable at the temperatures involved.

The results obtained with carbon dioxide and steam yield interesting information concerning the nature of the process of oxidation which has been briefly postulated. If the scaling losses at 1260 degrees Cent. for various times in an atmosphere of steam are divided by the scaling losses at the same temperature for the corresponding times in an atmosphere of carbon dioxide, it will be observed that the ratio of losses in the two atmospheres is approximately constant having a value of 2.5. The rates of these two reactions, of iron with steam, and of iron with carbon dioxide, must be proportional to the relative speeds of diffusion of the individual gases, to the effective driving force which enables diffusion to proceed and, according to Pfeil, to the rate of diffusion of iron. According to Graham's law of diffusion, the amount of gas diffusing through the

scale is expressed as follows: $D \propto \sqrt{\frac{1}{M}} \Delta\rho$

where M is the molecular weight of the diffusing gas and $\Delta\rho$ is the effective driving force causing diffusion. The loss in weight, W , will of course, be directly proportional to the amount of oxidizing gas diffusing inward and also to the amount of reducing gas diffusing outward and hence the loss in weight will be proportional to the product of the amounts of gases diffusing. The term $\Delta\rho$ is considered as the difference in concentration of the diffusing gas at the outside of the scale and its concentration at some point within the scale where equilibrium may be considered to have been established. The equilibrium concentrations of carbon dioxide and carbon monoxide and of steam and hydrogen in contact with iron and ferrous

oxide are given in Figs. 6 and 7. The driving force at 1260 degrees Cent. for the inward diffusion of carbon dioxide is $1.00 - 0.22$ or 0.78 since the gas outside the scale is pure carbon dioxide and since at the point where equilibrium is assumed, the concentration of carbon dioxide is 22 per cent or 0.22 mol fraction as read from Fig. 7. Likewise the driving force for the outward diffusion of carbon monoxide is $0.78 - 0$ or 0.78 since its concentration at the equilibrium point is 78 per cent or 0.78 mol fraction while in the atmosphere outside the scale its concentration is not greatly different from 0.

From this reasoning, omitting for the present any discussion of the diffusion of iron, the gaseous diffusion factors affecting loss in weight by scaling in carbon dioxide atmospheres may be formulated

as follows: $W \propto \sqrt{\frac{1}{CO_2}} \Delta p_{CO_2} \sqrt{\frac{1}{CO}} \Delta p_{CO}$ where W is the loss

in weight and CO and CO_2 represent the molecular weights of these gases. In this expression the relative speeds of diffusion of gaseous reagent and product and the driving force available to cause diffusion in each case occur. In a like manner the reaction with steam

may be formulated as $W \propto \sqrt{\frac{1}{H_2}} \Delta p_{H_2} \sqrt{\frac{1}{H_2O}} \Delta p_{H_2O}$. The expression for oxidation in carbon dioxide atmospheres becomes

$W \propto \sqrt{\frac{1}{44}} \times 0.78 \times \sqrt{\frac{1}{28}} \times 0.78$ when the molecular weights and

the proper values of Δp_{CO_2} and Δp_{CO} are substituted. When the indicated operations are performed $W \propto 0.0173$ at 1260 degrees Cent. for carbon dioxide oxidation. In the case of steam the expression

$W \propto \frac{1}{H_2} \times p_{H_2} \sqrt{\frac{1}{H_2O}} p_{H_2O}$ becomes $W \propto \sqrt{\frac{1}{2}} \times 0.56 \times$

$\sqrt{\frac{1}{18}} \times 0.56$ or $W \propto .0524$. On this basis it would appear that

the scaling losses in steam and carbon dioxide atmospheres should possess the ratio $\frac{0.0524}{0.0173}$ at 1260 degrees Cent. or 3.02. Actually it

was found that this ratio has a value of 2.5 which is somewhat lower than the calculated value indicating that the scaling in carbon dioxide was in reality more vigorous than the previous calculation would indicate.

Pfeil has suggested that the rate of scaling also depends on the rate of diffusion of iron outward through the scale. Thus far in the discussion only the diffusion of the gaseous reagents and products have been considered and it is seen that this does not lead to a complete correlation of the two sets of data. In order to account for the lower observed ratio of scaling losses in the two gases it will be necessary to introduce this third factor, namely the diffusion of iron. It

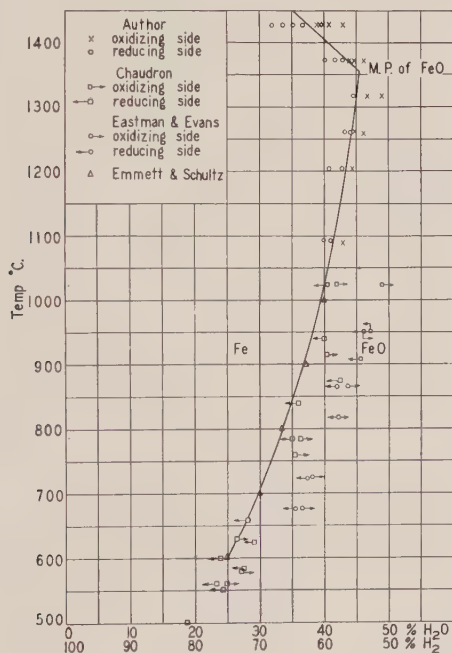


Fig. 6—Equilibrium Compositions for the System Fe-FeO-H₂-H₂O.

then appears probable that the effective rate of diffusion of iron through the scale instead of being equal in the two cases as was tacitly assumed in the previous formulation is somewhat greater in the case of oxidation with carbon dioxide than in the case of oxidation with steam. In fact it would be expected that the effective rates of diffusion of iron through oxides formed by carbon dioxide and in steam would be in the ratio of $\frac{3.0}{2.5}$ where 3.0 is the calculated ratio of loss in weight in steam to loss in weight in carbon dioxide and 2.5 is the observed

ratio of losses. The effective rate of diffusion of iron in the case of oxidation by carbon dioxide would thus be 1.2 times the effective rate of diffusion of iron in the case of oxidation with steam. It has been consistently observed in this research that the scale formed in carbon dioxide atmospheres adheres more tenaciously to the steel than does that formed in steam atmospheres. The tenacity of adherence of the scale to steel is at least partly dependent on the porosity of the

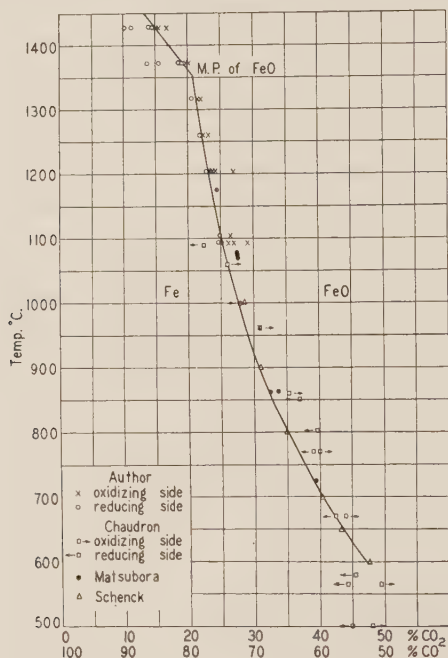


Fig. 7—Equilibrium Compositions for the System Fe-FeO: CO-CO₂.

scale so that the carbon dioxide scales would be somewhat less porous than the steam scales. This slight difference in porosity would allow for a slightly greater effective rate of diffusion of iron through the carbon dioxide scale than through the steam scale inasmuch as the area available for diffusion would be somewhat greater in the case of the carbon dioxide scales.

From the foregoing reasoning the effect of the diffusional properties of the gas is apparent. Since the diffusion of steam through the scale according to Graham's law will be more rapid than that of carbon dioxide, the oxide layers in the case of oxidation under water

vapor atmospheres will be more easily maintained in a state of unsaturation with respect to iron than in the case of carbon dioxide oxidation. This will allow a greater diffusion of iron and consequently a more rapid growth of the oxide layers. In addition, the gaseous product of oxidation of iron with steam possesses a more rapid rate of diffusion than does the gaseous product of oxidation with carbon dioxide, so that the presence of hydrogen in the first case will retard the reaction to a lesser degree than will the presence of carbon monoxide in the second case. It is evident, then, that the diffusion of reagent and product will operate so that the reaction with steam may proceed with considerably greater speed than that reaction with carbon dioxide.

The mechanism as now conceived involves the molecular diffusion of oxidizing gas inward and a diffusion of iron outward. The magnitude of the scaling effect at a given temperature during any time is at least partly dependent upon the relative speeds of diffusion of gaseous reagent and product. The magnitude of the effect is also dependent on the rate of diffusion of iron outward which has been postulated as being affected by the relative speeds of diffusion of gaseous product and reagent considering that the diffusion rate is dependent upon the ease with which the main portion of the scale is maintained in a state of unsaturation with respect to iron. The speeds of diffusion of gaseous reagent and product may likewise affect the maintenance of a metal oxide interface and consequently the rate of oxidation.

X-Ray Studies of Oxides

The similarity of the scales produced in carbon dioxide and steam is borne out by examination of the data derived from X-ray studies and summarized in Table IV which shows that there is no variation of lattice constant of either FeO or Fe_3O_4 with temperature or atmosphere. Wykoff²⁸ has given 4.29 Angstrom units as the constant of FeO, and 8.37 Angstrom units as the constant of Fe_3O_4 . Two oxides whose constants are of similar magnitude are shown to exist, one having a constant of 4.288Å and the other having a constant of 8.375Å. These may be identified as FeO and Fe_3O_4 by comparison with Wykoff's values. X-rays failed to reveal any distinct metallic iron lattice in these oxides. There seems to be no dis-

²⁸Wykoff, *The Structure of Crystals*; Chemical Catalogue Co.

Table IV
Variation of Lattice Constants and Chemical Composition of Oxides with Temperature.

Run No.	Atmosphere	Temperature Degrees Cent.	FeO Lattice Const.	Fe ₃ O ₄ Lattice Const.	% Fe	% FeO	% Fe ₃ O ₄
271	CO ₂	1149	4.287	8.379	0.13	61.5	37.7
276	CO ₂	1206	4.287		0.19	60.3	38.7
451	CO ₂	1260	4.287	8.379	0.13	59.0	39.6
521	CO ₂	1316	4.287		0.10	60.4	38.5
548	CO ₂	1371	4.286	8.379			
236	H ₂ O	1093	4.288	8.374	0.10	62.9	35.0
237	H ₂ O	1149	4.288		0.18	66.0	31.8
240	H ₂ O	1206	4.288	8.371	0.19	63.5	35.3
499	H ₂ O	1260	4.286	8.375	0.10	64.3	33.8
267	H ₂ O	1316	4.287		0.13	61.1	36.6
	H ₂ O-H ₂	1260	4.289				
	H ₂ O-H ₂	1427	4.289				

tortion of the FeO lattice so that the quantity of iron in solution in the oxide may be assumed to be very small. Chemical analysis has indicated the presence of 0.1 to 0.2 per cent metallic iron. Two samples of oxide which were produced with a slightly oxidizing mixture of hydrogen and steam, one at a temperature below the melting point and the other at temperature above the melting point, were photographed by means of X-rays. In the preparation of these two samples of oxide the atmospheres were so adjusted that no free ferro-ferric oxide could result from oxidation in the furnace since the mixtures of hydrogen and steam were only slightly oxidizing with respect to iron. Consequently, these samples should consist of nearly pure ferrous oxide since both were cooled extremely rapidly from the temperature of formation. It is possible then to place considerable reliance on the constant determined from these two samples of oxide which is 4.289Å. This is in good agreement with the value given by Wyckoff and cited previously. It has been mentioned that the lattice constants of FeO as given in Table IV show no variation with respect to temperature and atmosphere. It does not seem conceivable that large quantities of ferro-ferric oxide could dissolve in ferrous oxide without a considerable lattice distortion in view of the marked difference in lattice constants of the two oxides. From these facts there appears to be small possibility of extensive solid solution of ferro-ferric oxide or iron in ferrous oxide.

There has in the past been some idea that ferrous oxide lost its identity above the melting point. One sample of scale formed under an atmosphere of carbon dioxide at 1370 degrees Cent. (2500 degrees Fahr.) which is definitely above the melting point, and another sam-

ple obtained at 1425 degrees Cent. (2600 degrees Fahr.) with an atmosphere of hydrogen and water vapor so adjusted as to be slightly oxidizing, were subjected to X-ray analysis. The results appear in Table IV. When the values of the constants of these two samples are compared with those formed below 1370 degrees Cent. (2500

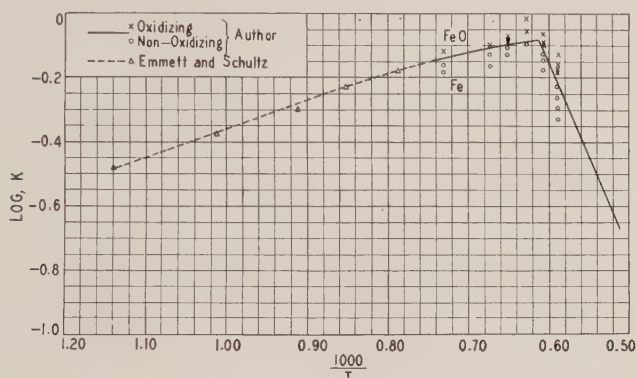


Fig. 8—Equilibrium Constants on the Fe-O-H System at Temperatures up to 1427 Degrees Cent. (2600 Degrees Fahr.).

degrees Fahr.) there can be no doubt that the lattice constant of ferrous oxide has undergone no alteration by reason of having been formed in the molten state. It, therefore, seems reasonable to assert that ferrous oxide is stable above its melting point. This point is of considerable interest in view of the equilibrium data which was obtained in this research.

Equilibria in the Systems Fe:O:H and Fe:O:C

During the course of the investigation it appeared that the methods which had been developed for the determination of rates of scaling could also be applied to the extension of the data on the systems Fe: FeO: H₂: H₂O and Fe: FeO: CO: CO₂ to higher temperatures than had previously been used. The basis of the adaptation of the scaling methods to equilibrium determinations is that at any temperature the true composition of a gaseous phase in equilibrium with a solid phase consisting of Fe and FeO must lie between two gas phase compositions of which one produces oxidation of iron and the other does not. If the gas phase has a sufficient velocity, the effect of each type of atmosphere on iron may be ascertained without reference to the composition of the gases after contact with the sample. An atmosphere which contains slightly more than the neces-

sary amount of reducing agent required to prevent scaling will of course result in no oxidation, while an atmosphere that contains slightly less than the necessary amount of reducing agent required to prevent scaling will result in oxidation of the sample. The complete curve is drawn, as shown in Figs. 6, 7, 8, and 9, so that at all temperatures it lies within the narrowest range between oxidizing and non-oxidizing compositions of the atmosphere. The range of

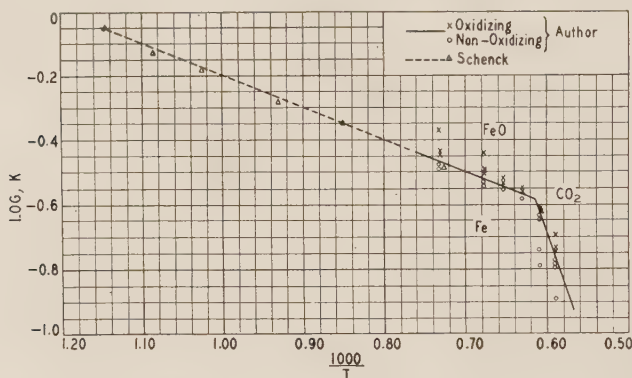


Fig. 9—Equilibrium Constants on the Fe-C-O System at Temperatures up to 1427 Degrees Cent. (2600 Degrees Fahr.).

composition between oxidizing and non-oxidizing atmospheres, may, of course, be within any desired limits. It must be remembered, however, that the narrower the range, the more time will be necessary to establish the effect of any certain atmosphere on iron since the rate of oxidation as the true equilibrium composition is approached becomes very slow.

It is apparent from Figs. 6 and 7 in which the gas composition is plotted against temperature in degrees Centigrade, that the data for these two systems furnish an excellent check on the work of Emmett and Schultz¹⁰ in the Fe:O:H system and on the researches of Schenck¹³ in the Fe:O:C system. For comparison with the work of other authors the results of some researches have been plotted. It will be observed that Eastman and Evans¹³ data on the Fe:O:H systems which it may be said agree generally with that of Schreiner and Grimmes²⁰ and that of Wohler³⁰ are definitely in the oxide region

²⁰Schreiner and Grimmes, *Zeitschrift fuer Anorganische und Allgemeine Chemie*, Vol. 110, 1920, p. 311.

³⁰Wohler, et al., *Zeitschrift fuer Elektrochemie und Angewandte Physikalische Chemie*, Vol. 23, 1917, p. 119; Vol. 27, 1921, p. 406; Vol. 29, 1923, p. 226.

Table V
Scaling and Non-scaling Mixtures of Carbon Dioxide and Carbon Monoxide at
Temperatures of 1093 to 1427 Degrees Centigrade.

Run No.	Temperature Degrees Cent.	Per Cent CO ₂	Condition of Sample After Testing	Equil. Const.	-Log K
				K = $\frac{\text{PCO}_2}{\text{PCO}}$	
54	1093	29.2	Scaled	0.413	0.384
34	1093	27.0	Scaled	0.370	0.432
33	1093	26.9	Scaled	0.368	0.434
35	1093	26.4	Scaled	0.358	0.446
59	1093	25.3	Not Scaled	0.339	0.470
60	1093	24.8	Not Scaled	0.330	0.481
44	1102	26.5		0.360	0.444
56	1104	25.0		0.333	0.477
38	1204	27.0	Scaled	0.370	0.432
36	1204	24.3	Scaled	0.321	0.493
39	1204	23.7	Scaled	0.311	0.507
62	1204	23.6	Scaled	0.309	0.510
37	1204	22.9	Not Scaled	0.297	0.527
66	1204	22.8	Not Scaled	0.295	0.530
40	1260	23.2	Scaled	0.302	0.520
64	1260	22.4	Scaled	0.289	0.539
41	1260	22.0	Not Scaled	0.282	0.550
65	1260	22.0	Not Scaled	0.282	0.550
43	1316	22.0	Scaled	0.282	0.550
50	1316	21.4	Scaled	0.272	0.565
42	1316	20.6	Not Scaled	0.260	0.585
52	1371	20.0	Scaled	0.250	0.602
68	1371	19.6	Scaled	0.244	0.613
67	1371	19.1	Not Scaled	0.236	0.627
51	1371	18.7	Not Scaled	0.230	0.638
46	1371	15.5	Not Scaled	0.183	0.738
47	1371	13.8	Not Scaled	0.160	0.796
53	1427	16.7	Scaled	0.200	0.699
55	1427	15.5	Scaled	0.184	0.735
69	1427	15.1	Scaled	0.178	0.750
70	1427	14.6	Not Scaled	0.171	0.767
58	1427	14.3	Not Scaled	0.167	0.777
71	1427	14.0	Not Scaled	0.163	0.788
48	1427	11.3	Not Scaled	0.121	0.896
49	1427	10.2	Not Scaled	0.114	0.943

according to the data presented in this paper and that presented by Emmett and Schultz. The results of Chaudron³¹ which are characteristic of the group of authors who found lower values of the equilibrium constant $p\text{H}_2\text{O}/p\text{H}_2$ are not so very different from those of Emmett and Schultz. For the Fe:C:O system, the data of Matsubara¹¹, of Schenck, and of Chaudron³², are plotted in Fig. 7. In general their results are not widely different but our data obtained at high temperatures and shown in Table V are in better agreement with Schenck's latest values, and, hence, his values have been used as the lower extension of the diagram in the Fe:C:O system.

In the description of methods previously used by investigators of such systems it will be noted that with few exceptions the method

³¹Chaudron, *Comptes rendus*, Vol. 159, 1914, p. 237; *Ann. chem. phys.*, Vol. 16, 1921, p. 221.

³²Chaudron, *Comptes rendus*, Vol. 172, 1921, p. 152.

employed has been a so-called static one. The principal exceptions are Emmett and Schultz who devised an excellent flow method for the $\text{Fe}:\text{O}:\text{H}$ system, and whose results, it has been observed, furnish an excellent basis for the indirect calculation of water-gas constants. Emmett and Schultz have advanced the hypothesis that certain surface phenomena in the case of the $\text{Fe}:\text{O}:\text{H}$ system gave rise to abnormal or false equilibria in the static methods which were exceedingly difficult to correct. On the basis of the variables which influence the mechanism of oxidation, and which have been discussed, there are possibly two other sources of difficulty in the static methods. One is based on the fact that in these methods the circulation of gas is very slow at the best, and, hence, when any abnormal reaction has occurred at the solid surface, the correction of this condition may be extremely difficult on account of the slowness of the reaction at low velocities; hence, false equilibria would be rendered easy to attain. The other possible difficulty arises from the fact that in this method as applied to the $\text{Fe}:\text{O}:\text{H}$ system low pressures were used which also tended to retard the speed of any reaction which might have begun. Both the velocity and pressure factors operate in such a way that the reaction is rendered slow, probably much more so than many authors believed, so that the attainment of a true equilibrium would require a long time if any reactions had occurred with abnormal intensity at the beginning. Although many investigators have claimed that they have positively approached equilibrium from both directions, a consideration of their results in view of the evident slowness of the reaction under the condition with which they worked renders the truth of this assertion doubtful. Certainly, the conditions of many experiments was such that an abnormal reaction at the start might never be corrected in a reasonable length of time. With the flow methods at atmospheric pressure the reactions are much intensified and their true direction easily ascertained.

The melting point of the oxide is shown as a definite discontinuity at 1360 degrees Cent. in the curves of the composition temperature diagrams in Figs. 6 and 7. For both the $\text{Fe}:\text{C}:\text{O}$ and $\text{Fe}:\text{H}:\text{O}$ systems this discontinuity occurs at nearly the same temperature so there is reason to believe that the discontinuity arises from the same source, the melting of FeO , in both cases. Of course, there are several possible positions for a line drawn within the range between the oxidizing and non-oxidizing atmospheres at 1370 degrees

Cent. and 1425 degrees Cent. (2500-2600 degrees Fahr.) and in each of these positions the line would intersect the curve for solid FeO at a slightly different temperature so that the melting point can be considered as 1360 degrees Cent. $\pm$ 5 degrees Cent. (2480 degrees Fahr. $\pm$ 9 degrees Fahr.) excluding the inherent errors of temperature measurement which have already been cited. The identity of the oxide both above and below the melting point has already been established on the basis of the X-ray diagrams which formed a part of this work.

The heat of fusion of ferrous oxide may be calculated from our data. In Figs. 8 and 9 the values of log K have been plotted against $1/T$, when K is $p\text{H}_2\text{O}/p\text{H}_2$ or $p\text{CO}_2/p\text{CO}$, and T is degrees absolute. The curves in these figures have likewise been drawn so that at all temperatures they lie within the range between oxidizing and non-oxidizing atmospheres. The thermodynamic formula $\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}$, where ΔH is the heat of reaction, and R the universal gas constant, is employed to find the heat of fusion. This may be rewritten,

$$\frac{\frac{d \ln K}{dT}}{T^2} = \frac{\Delta H}{R}, \text{ or } \frac{d \ln K}{d\left(\frac{1}{T}\right)} = \frac{-\Delta H}{R}$$

The heat of reaction then is simply the slope of the $\ln K - \frac{1}{T}$ curve at any point multiplied by R. If the heats of reaction in the direction $\text{FeO} + \text{H}_2 = \text{Fe} + \text{H}_2\text{O}$ or $\text{FeO} + \text{CO} \rightleftharpoons \text{Fe} + \text{CO}_2$ are determined at the melting point, one being derived from the curve for solid FeO and the other from the curve for liquid FeO, the difference between these heats of reaction is attributed to the absorption of energy in causing FeO to liquefy. These calculations have accordingly been carried out for both systems and yield the following results:

Fe:H:O below melting point $\Delta H = +2300$ cal/gm mol
 Fe:H:O above melting point $\Delta H = -26600$ cal/gm mol
 Heat of fusion of FeO = + 28900 cal/gm mol
 Fe:C:O below melting point $\Delta H = -4600$ cal/gm mol
 Fe:C:O above melting point $\Delta H = -31300$ cal/gm mol
 Heat of fusion of FeO = + 26700 cal/gm mol

The values of the heat of fusion check to 2200 cal., the average being +28000 calories per gram mol. However, since the same error is resident in drawing the curves above the melting point, namely the fact that a line drawn within the range between oxidizing and non-oxidizing atmospheres may occupy several positions, this value of +28000 calories can be considered correct only to ± 5000 calories. As far as is known these are the only data secured at sufficiently high temperatures to permit a calculation of the heat of fusion.

In summing up previous work C. H. Herty, Jr.⁹ has given 1355 to 1370 degrees Cent. (2470-2500 degrees Fahr.) as the melting point of ferrous oxide, and the result previously given based on discontinuities of curves yields 1360 degrees Cent. which is in good agreement with the values presented by Herty.

Scaling in the Products of Combustion of Gas

When city gas and air are burned, the city gas being in excess, carbon dioxide, carbon monoxide, steam and hydrogen are present in the products of combustion. These will adjust themselves in amount to conform to the water-gas constant for the particular temperature. In calculating the water-gas constant indirectly from the Fe:O:H and Fe:C:O systems the ratios H_2O/H_2 and CO_2/CO are combined so that a non-scaling mixture of the four gases will be required to possess certain ratios of H_2O/H_2 and CO_2/CO while an oxidizing mixture will have other values for these ratios. For instance at 1260 degrees Cent. (2300 degrees Fahr.) the ratio of CO_2/CO has a value 0.288, while the ratio H_2O/H_2 has a value of 0.792, both for non-scaling atmospheres. Those atmospheres in which these ratios are greater in value at this temperature than the values just given will produce oxidation.

In Table VI various data are presented for scaling and non-scaling experiments at 1260 degrees Cent. (2300 degrees Fahr.) in atmospheres consisting of the products of combustion of city gas and air. This table shows for a number of steels that atmospheres which yield ratios in excess of those read from the equilibria data of the two systems produce oxidation, while those atmospheres which yield ratios whose value is less than those from the equilibria data produce no oxidation. This apparently holds true for a fairly wide range of steels, but the adjustment of atmosphere has not in most cases been sufficiently close to determine whether or not the equilibria

Table VI

Comparison of CO₂-CO and H₂O-H₂ Ratios for Scaling and Non-scaling Tests on Various Steels at 1260 Degrees Cent. All Runs 40 Minutes.

Run No.	Steel	K ₁ =	PCO ₂	K ₂ =	PH ₂ O	Condition After Testing
			PCO		PH ₂	
A1-19	1030		0.346		0.879	Scaled
A1-20	1030		0.199		0.479	Not Scaled
A2-15	1050		0.346		0.880	Scaled
A2-17	1050		0.199		0.579	Not Scaled
A3-10	1090		0.675		1.85	Scaled
A3-16	1090		0.199		0.479	Not Scaled
E-15	1.12%C		0.333		0.875	Scaled
E-17	1.12%C		0.337		0.310	Not Scaled
FF-14	2320		0.450		1.07	Scaled
FF-15	2320		0.238		0.639	Not Scaled
G-14	3130		0.431		1.07	Scaled
G-16	3130		0.219		0.495	Not Scaled
Q-21	6145		0.420		1.05	Scaled
Q-15	6145		0.238		0.639	Not Scaled
L-11	4615		0.610		1.36	Scaled
L-14	4615		0.304		0.670	Not Scaled
KK-14	4140		0.530		1.47	Scaled
KK-3	4140		0.300		0.520	Not Scaled
YY-13	High Speed		0.354		0.803	Scaled
YY-15	High Speed		0.238		0.639	Not Scaled

Value % CO₂/ % CO ratio from Figure 7 0.288 at 1260 Degrees Cent.

Value % H₂O/ % H₂ ratio from Figure 6 0.792 at 1260 Degrees Cent.

data can be applied to steels having high alloy contents. It is true, however, that the data on the Fe:H₂O and Fe:C₂O systems, which have in this research been extended to 1425 degrees Cent. (2600 degrees Fahr.) can be used as a general guide to determine the probable effect of a certain atmosphere on steel at any chosen temperature. It should be remembered, however, that application of these data is conditioned upon the combustion gases attaining equilibrium before the surface of the steel is reached; without this condition obtaining the effect of any atmosphere must necessarily be uncertain.

While most of the variables operative in the oxidation of steel have been discussed here it is appreciated that there are some which have not been touched. Among these are the effect of surface conditions of the steel and the effect of elements other than carbon occurring in the steel as well as the special elements appearing in alloy steels. Further information concerning the rate of diffusion of iron through oxides and the factors affecting this diffusion as well as information regarding the rates of diffusion of various gases through oxides would prove highly interesting. Until such data are available over a considerable temperature range it will not be possible to outline a complete theory regarding the process of oxidation.

Further research in the equilibria of the systems Fe: FeO: H₂: H₂O and Fe: FeO: CO: CO₂ particularly above the melting

point of the oxide and above the temperatures attained in this investigation would aid considerably in establishing more definitely the heat of fusion of the oxide and the phase boundaries.

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